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TRANSLATION

ON THE QUESTION OF HEAT AND MASS TRANSFER AT THE FORWARD
POINT OF BLUNT BODIES IN THE PRESENCE OF HETEROGENEOUS
CHEMICAL REACTIONS

By

V. P. Motulevich

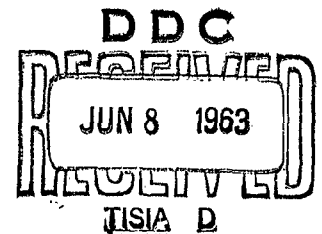
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ON THE QUESTION OF HEAT AND MASS TRANSFER AT THE
FORWARD POINT OF BLUNT BODIES IN THE PRESENCE
OF HETEROGENEOUS CHEMICAL REACTIONS

V. P. Motulevich

Considered in the paper is the heat and mass transfer of a blunt body in an incompressible fluid flow in the presence of heterogeneous reactions of the most general type occurring at finite rate. Analyzed are the questions of ignition and extinction, as well as the dependence of the intensity of mass removal and surface temperature on the various parameters characterizing the body, the flow, and the chemical reactions occurring.

The evolution of a number of new engineering fields has made it necessary to devote attention to convective heat transfer between a fluid flow and body in the presence of chemical processes taking place in the flow itself and on the surface of the body. This problem is encountered beginning with the study of combustion processes and ending

with the interaction of bodies with flows of high velocity and high temperature.

A considerable number of papers dealing with these problems [1-3] have recently appeared.

The aim of the present investigation is a theoretical analysis of the processes of heat and mass transfer, taking into account heterogeneous chemical reactions on the rate of which no restrictions are placed.

1. Formulation of the Problem

We shall consider a certain plane or axisymmetrical body in a flow of multi-component gas A, capable of entering into a chemical reaction with the material of the body B, as a result of which a gaseous product C is formed. Neutral gases may also be present in the flow in addition to the reacting components.

The body material is generally a finely dispersed mechanical mixture consisting of l components, the grains of which are sufficiently small in comparison with the characteristic dimensions of the body.

Because of the different rates of removal of the individual components of the body, the originally smooth surface of the latter may become rough, whereupon the flow at the wall acquires a complex turbulent character, thus making the problem exceedingly complicated.

The boundary layer surrounding the body is a multicomponent mixture existing under conditions of concentration, temperature, and pressure gradients.

Thus an analysis of the problem in an exact formulation even in the case of laminar flow makes it necessary to consider the system of complicated equations presented by Motulevich [4].

In the present article a number of simplifications relating to the properties of the gases and to the characteristics of the flow are introduced, viz:

1. The flow occurs in the neighborhood of the forward critical point.
2. The flow is laminar.
3. The fraction of the surface occupied by the individual components of the solid material, $\phi_1 = s_1/s$, does not change with time.
4. The thermodynamic and gaskinetic parameters of the fluid are constant, and the diffusion coefficients D_K are the same for all components of the mixture; $Pr = Le = 1$.
5. Only concentration diffusion is considered.
6. The wall is adiabatic.
7. The effect of "contamination" of the surface by the reaction products due to the adsorption of the latter, as well as the effect of the reaction's occurring partially inside the porous wall, are assumed to be insignificant.

2. Initial System of Equations

We shall make the x-axis pass along the contour of the body, beginning at the forward point, and make the y-axis perpendicular to the x-axis.

Then, if instead of x and y we introduce the new variables:

$$\xi = \rho_0 \left(\frac{du_\infty}{dx} \right)_0 \frac{x^{2(\alpha+1)}}{2(\alpha+1)}; \quad \eta = y \sqrt{\frac{\rho}{\mu} \left(\frac{du_\infty}{dx} \right)_0 (\alpha+1)}, \quad (1)$$

where $\alpha = 0$ for flat bodies and $\alpha = 1$ for axisymmetrical bodies, while $(du_\infty/dx)_0$ is the velocity gradient of an inviscid flow at the frontal point, the momentum and energy equations for the boundary layer may be converted to the form:

$$f''' + ff'' + \frac{1}{x+1}[1 - (f')^2] = 0, \quad (2)$$

$$\bar{T}'' + f\bar{T}' = 0, \quad (3)$$

$$f = -\frac{0.2}{\sqrt{\mu_0 \left(\frac{du_\infty}{dx} \right)_0 (x+1)}}; \quad f' = \frac{u}{u_\infty}; \quad (4)$$

$$\bar{T} = \frac{T - T_w}{T_\infty - T_w} \quad (5)$$

and all the variables are functions only of η^* .

Solutions to Eq. (2) may be obtained numerically for different f_w (in particular, this problem has been solved for the plane case by Schlichting [5], so that the function $f = f(\eta, f_w)$ may be considered known).

Equation (3) is solved in quadratures [5]; from the solution it is not difficult to obtain

$$\bar{T}_w = \left[\int_0^\infty \exp \left(-\int_0^\eta f d\eta \right) d\eta \right]^{-1} = \bar{T}_w(f_w). \quad (6)$$

Since $Le = 1$, the temperature and concentration profiles are similar, i.e.,

$$(T - T_w)/(T_\infty - T_w) = (k_i - k_{iw})/(k_{i\infty} - k_{iw}), \quad (7)$$

where k_i is the part by weight of the i -th component of the mixture.

In general, each of the l components of the surface may take part in m_l reactions of the type

$$\sum_i \nu_{im_l} A_i + \nu_{lm_l} B_l = \sum_k \nu_{km_l} C_k, \quad (8)$$

* Commonly used notations and subscripts will not be explained.

where ν are stoichiometric coefficients, and the subscripts i , k , and l pertain respectively to the initial and final gaseous products and to the solid body. Since the wall is adiabatic, we may write

$$\left(\lambda \frac{\partial T}{\partial y} \right)_w = r_{av} (\rho v)_w, \quad (9)$$

where r_{av} is the average heat of reaction of the surface material and is determined by the expression ($r > 0$ for an endothermic reaction):

$$r_{av} = \frac{\sum_i \varphi_i \sum_{m_i} r_{m_i} (\rho v)_{m_i}^*}{\sum_{m_i} (\rho v)_{m_i}^*}, \quad (10)$$

while

$$(\rho v)_{m_i}^* = (\rho v)_{m_i} / (\rho v)_w. \quad (11)$$

The equation of the preservation of a component on the wall may be presented in the form

$$k_w (\rho v)_w - \rho D \left(\frac{\partial h}{\partial y} \right)_w = (\rho v)_w \sum_i \varphi_i \sum_{m_i} (\rho v)_{m_i}^* \theta_{m_i}, \quad (12)$$

where θ_{m_l} is the fraction of the substance A or C generated in a reaction with a unit mass of the substance B_1 , for example

$$\theta_{im_l} = -\nu_{im_l} m_l / \nu_{lm_l} m_l, \quad (13)$$

where m is the molecular weight.

The rate of generation of a substance on the surface during a reaction is determined in the general case by the expression

$$(\rho v)_{m_l} = z_{m_l} \prod_i \left(\frac{\rho}{m_i} k_{iw} \right)^{\nu_{im_l}} \left[1 - K_{m_l} \frac{\prod_k \left(\frac{\rho}{m_k} k_{kw} \right)^{\nu_{km_l}}}{\prod_i \left(\frac{\rho}{m_i} k_{iw} \right)^{\nu_{im_l}}} \right], \quad (14)$$

where n is the order of the reaction; K is the equilibrium constant, the temperature dependence of which is assumed to be known; κ is the temperature coefficient of the forward reaction, which may be determined using Arrhenius' law

$$z_{m_l} = z_{m_l} \exp \left(-\frac{A_{m_l}}{RT_w} \right), \quad (15)$$

where \underline{z} is the kinetic constant, and A is the activation energy.

Equations (14) and (15) should in general be considered not as absolutely rigorous equations but as expressions whose form characterizes sufficiently well the experimentally observed dependence of the rate of reaction on the concentration of the reacting components and the temperature.

In addition, it should be noted that Eq. (13) is strictly valid only if the substance B_1 generated in the reverse reaction is completely precipitated on the surface.

Using the relationships presented, it is possible through simple transformations to obtain a closed system of equations, the solution to which will give the answer to all questions which can arise within the framework of the formulated problem:

$$\bar{T}_w(-\bar{m}) = \bar{r}_{av} \bar{n}, \quad (16)$$

$$\bar{r}_{av} = \frac{r_{av}}{c_p(T_\infty - T_w)}, \quad (17)$$

$$k_w = \frac{k_\infty \bar{r}_{av} + \sum_i \varphi_i \sum_{m_i} \frac{\theta_{m_i}}{m_i} (\varphi \vartheta)_{m_i}^*}{1 + \bar{r}_{av}}, \quad (18)$$

$$\begin{aligned} \bar{r}_{m_i}^* &= \frac{r_{m_i} \prod_i \left(\frac{\varphi}{m_i} k_{i\infty} \right)^{n_{im_i}}}{\sqrt{\varphi^u \left(\frac{du}{dx} \right)_0 (\alpha + 1)}} \times \\ &\times \left[1 - K_{m_i} \frac{\prod_k \left(\frac{\varphi}{m_k} k_{k\infty} \right)^{n_{km_i}}}{\prod_i \left(\frac{\varphi}{m_i} k_{i\infty} \right)^{n_{im_i}}} \right]. \end{aligned} \quad (19)$$

$$\bar{r}_{m_i}^* = (\varphi \vartheta)_{m_i}^* \bar{m}, \quad (20)$$

$$\sum_{i,j,k} k_w = 1, \quad (21)$$

where \bar{m} is a dimensionless parameter characterizing a material-removal rate proportional to the quantity supplied heat:

$$\bar{m} \equiv -\dot{f}_w = (\gamma v)_w / \sqrt{\gamma^2 (du_\infty/dx)_0^2 (\alpha + 1)}; \quad (22)$$

γ^* is a parameter characterizing the material removal resulting from the chemical reaction.

In the system presented the solution to the differential equations is necessary only in order to obtain relationship (16), it being of a universal nature and independent of the flow and body parameters and the kinetics of the reaction.

Thus the problem reduces essentially to the solution of a system of algebraic equations, a solution which can be found only by numerical methods.

3. A Homogeneous Body in the Presence of One Irreversible Reaction

An analysis of the obtained system in its general form is difficult; it will be simpler and easier to visualize, if we analyze it for the case characterized in the title of the present section. A number of the qualitative conclusions thus obtained will be of general significance.

In the case in question the initial system of equations is obtained from the general system, in it we set

$$\varphi_i = (\gamma v)_{m_i}^* = 1; \quad K_{m_i} = 0,$$

which makes it possible to write:

$$\bar{m} = \bar{m}(\bar{r}), \quad (16a)$$

$$\bar{r} = r/[c_p(T_\infty - T_w)], \quad (17a)$$

$$k_{iw} = (k_{i\infty} \bar{r} + \theta_i)/(1 + \bar{r}), \quad (18a)$$

$$\gamma^* = \gamma \{ \gamma (k_{i\infty} \bar{r} + \theta_i) / [m (1 + \bar{r})] \}^{\alpha} \sqrt{\gamma^2 \left(\frac{du_\infty}{dx} \right)_0^2 (\alpha + 1)} \times$$

$$\times \exp \left(A / \left[R \left(T_{\infty} - \frac{r}{\bar{r} c_p} \right) \right] \right) \right]^{-1}, \quad (19a)$$

$$\gamma^* = \bar{m}. \quad (20a)$$

a) On the Limiting Values of Some of the Parameters. An analysis of the obtained system permits a number of preliminary conclusions to be drawn before solving the system:

1. The concentration of the initial products at the wall does not depend explicitly on the kinetics of the reaction, the velocity of the flow, the shape and dimensions of the body, etc., and for the given reaction is determined solely by the thermal head.

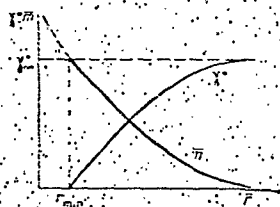


Fig. 1. Solution for the case of an endothermic reaction.

2. Since $k_{1w} > 0$, according to (16a) and (18a), there exists $\bar{r}_{\min} = -\frac{\theta_1}{k_{1\infty}} > 0$ and a value \bar{m}_{\max} concomitant with it. (Fig. 1)

3. Equation (17a) attests to the existence of extremum value of the temperatures of the reacting surfaces. They may vary from the temperature of the ambient medium up to a maximum in the case of an exothermic reaction and to a minimum in the case of an endothermic reaction; these extremums may be determined from the general formula

$$T_w = T_{\infty} + \frac{k_{i\infty} r}{c_p \theta_i}. \quad (23)$$

4. Since in the case of an endothermic reaction $T_{w \min} > 0$, we can conclude from Eqs. (18a) and (23) that in this case there exists

$$k_{i\infty \min} = \frac{k_{i\infty} r + \theta_i c_p T_{\infty}}{r + c_p T_{\infty}}. \quad (24)$$

b) On the Stability of the Solution. It follows from Eq. (20a) that the solution corresponds to the point of intersection or tangency of the curves of the functions $\bar{m} = \bar{m}(\bar{r})$ (16a) and $\gamma^* = \gamma^*(\bar{r})$ (19a).

Of all the possible solutions only the stable ones are of practical interest; in the event of small deviations from them the system returns spontaneously to its original state.

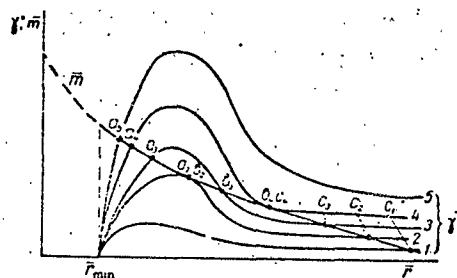


Fig. 2. Solutions for the case of an exothermic reaction.

It is not difficult to show that the stable regime exists if

$$d\bar{\gamma}/d\bar{r} \leq d\bar{\gamma}^*/d\bar{r}, \quad (25)$$

In the case of an equality the solution will be stable only on the side where inequality (25) is fulfilled.

c) The Possible Types of

Solutions for exo- and endothermic reactions are shown schematically in Figs. 1 and 2.

The difference in the behavior of the curves $\gamma^* = \gamma^*(\bar{r})$ is explained by the fact that with an increase in \bar{r} in the case of an endothermic reaction k_{1w} (18a) and T_w also increase while in the case of an exothermic reaction an increase in k_w is accompanied by a decrease in T_w , so that the curve $\gamma^* = \gamma^*(\bar{r})$ passes through a maximum.

As is apparent from Fig. 1, in the case of an endothermic reaction there exists only one solution, it being a stable one.

Presented in Fig. 2 are five different variants of the respective positions of the curves $\bar{m} = \bar{m}(\bar{r})$ and $\gamma^* = \gamma^*(\bar{r})$.

The first curve pertains to the "cold" reaction regime. There is only one stable solution (the point c_1).

On a curve of the second type two solutions are possible: a stable "cold" solution (point c_2) and a "hot" solution (merged points a_2 and b_2), stable only on the high-temperature side (extinction regime).

The third curve is the most general. Here three solutions are possible: a stable "hot" solution (point a_3), an unstable "intermedi-

ate" solution (point b_3), and a stable "cold" solution (point c_3).

On a curve of the fourth type two solutions are possible: a stable "hot" solution (point a_4) and a "cold" solution (merged points b_4 and c_4) stable only on the side of lower temperatures (ignition regime).

Finally, the fifth curve corresponds to the case in which there exists only the stable "hot" solution (point a_5).

d). Ignition and Extinction Regimes are conveniently analyzed with the aid of Fig. 2.

Let the initial gas temperature T_∞ of the incident flow be so low that the function $\gamma^* = \gamma^*(\bar{r})$ is characterized by a curve of type 1. In this case there will exist one stable regime with a low surface temperature and a low mass-removal intensity (point c_1).

It follows from Eq. (19a) that with an increase in T_∞ we will move to the curves in Fig. 2 that are of high numerical order. In this case the wall temperature and the mass-removal intensity will gradually increase, remaining nevertheless relatively small. The regimes will be stable until we reach an incident-flow temperature T_{ig} , which corresponds to a curve of type 4.

In this case it is enough for a slight accidental increase in the temperature of the wall or flow to occur, and the heat generation due to the reaction will exceed the heat removal by heat conduction, the wall will begin to heat up intensely, and the system will rapidly pass into a new stable state, characterized by much higher values of the surface temperature and mass-removal intensity. Further increase in the incident-flow temperature leads only to a slight increase in these parameters.

Analogously, it is possible to predict the phenomenon of extinction and to introduce the extinction temperature T_{ex} which corresponds to a curve of type 2.

We should mention that, generally speaking, when the process does not take place in a uniform way ignition may also occur when $T < T_{ig}$, and extinction may occur when $T > T_{ex}$.

An analysis of Fig. 2 shows that the ignition temperature is always greater than the extinction temperature. This can be seen especially clearly along the hysteresis loop formed when the wall temperature is plotted as a function of the incident-flow temperature in the case of a successive increase and decrease in the latter (Fig. 3).

An analysis of curves 2 and 3 in Fig. 2 indicates that in order to find T_{ig} and T_{ex} it is necessary to solve the system of equations:

$$m = \gamma^*, \quad (26)$$

$$d\bar{m}/d\bar{r} = d\gamma^*/d\bar{r}. \quad (27)$$

Evaluating \bar{m} and γ^* with the aid of Eqs. (22) and (19a), we obtain equations in two unknowns: \bar{r} and T_∞ , the latter having two solutions of which the greater corresponds to T_{ig} and the lesser to T_{ex} .

It follows from the equations presented that the ignition and extinction temperatures are not only functions of the chemical characteristics of the reacting substances; the velocity and density of the incident flow, as well as the dimensions and shape of the body in the flow play an essential role.

We shall make use of Fig. 2 for a qualitative analysis of the dependence of the transient temperatures on various parameters. Obviously, if a change in any parameter leads to a move to a curve $\gamma^* = \gamma^*(\bar{r})$ with a higher numerical order (i.e., to higher values of γ^* ,

all other things being equal), then it will cause a decrease in the flow temperatures corresponding to both transient regimes. A decrease in γ^* leads to the opposite effect.

Thus an analysis of Eq. (19a) enables us to determine the causes of an increase in the transient temperatures. These causes are:

1. An increase in (du_{∞}/dx) , i.e., an increase in the blow-off velocity a decrease in the dimensions of the body, and a streamlining of the body.
2. A decrease in the density ρ , when $n > 0.5$, and an increase in it, when $n < 0.5$. It should be noted that in our problem the effect of a change in the density is to some degree analogous to the effect of a change in pressure for a flow of compressible fluid.
3. A decrease in the kinetic constant \underline{z} .
4. An increase in the activation energy A .
5. A decrease in the absolute value of the heat of reaction \underline{r} .
6. A reduction of the concentration of the initial component in the incident flow $k_{i\infty}$.

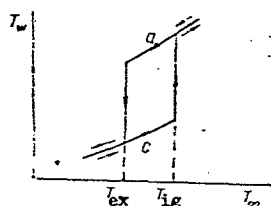


Fig. 3. Dependence of surface temperature on flow temperature in exothermic reactions.

The reverse changes lead to a decrease in the ignition and extinction temperatures.

e) Analysis of the Effect of Various Factors on the Basic Characteristics of the Process. Usually the rate of disintegration of the surface, its temperature, and, to a lesser degree, the concentration of the initial components close to it are of the keenest

practical interest.

The graphs plotted above and an analysis of Eqs. (17a), and (19a), and (22) enable us, in the majority of cases, to give a qualitative

(and when the plotting is accurate a qualitative) answer to the question of the effect of the various parameters of the flow and of the body located in the flow on these characteristics of the process.

For all types of reactions an increase in the incident-flow temperature leads to an increase in the mass removal and the surface temperature and to a decrease in the concentration of the initial products at the wall.

An increase in density leads to an increase in the material removal; when $n < 0.5$, k_{iw} increases and T_w increases in endothermic reactions; when $n > 0.5$, k_{iw} and T_w behave in the opposite way.

With an increase in $(du_\infty/dx)_0$ the material removal increases, and k_{iw} increases, while T_w increases for endo- and decreases for exothermic reactions.

It should be remembered that we are not allowing for radiant heat transfer which in some cases may play an appreciable role and even lead to qualitatively different results; in particular, in exothermic reactions with an increase in the blow-off velocity T_w may increase instead of decreasing.

An increase in the absolute value of the heat of reaction in the case of endothermic reactions leads to a decrease in material removal, an increase in k_{iw} , and a decrease in T_w ; the variation in these parameters is just the opposite for exothermic reactions.

An increase in the kinetic constant \underline{z} and a decrease in the activation energy A always cause an increase in material removal, a decrease in k_{iw} , and an increase in the wall temperature for exothermic reactions and a decrease in T_w for endothermic reactions.

An increase in the concentration of the initial components in an undisturbed flow leads to an increase in material removal, and a

decrease in T_w in the case of endothermic reactions and an increase in T_w for exothermic reactions; as regards k_{iw} , it increases during endothermic reactions, but it is impossible to determine the nature of its variation during exothermic reactions until actual qualitative calculations are performed.

4. The Effect of Reversibility of Chemical Reactions

When reversible reactions take place, the initial system of equations remains the same. The only difference will be that in place of γ^* determined from Eq. (19a), it will be necessary to take γ_m^* (Eq. 19)) and also to supplementarily use the known dependence of the equilibrium constant on the temperature.

The technique of analyzing the system and the principal qualitative conclusions remain the same.

From Eqs. (19) and (19a) it follows that

$$\dot{\gamma}_m < \dot{\gamma} \quad (28)$$

An analysis of Figs. 1 and 2, together with inequality (28), shows that taking reversibility into account in reactions of any type leads to a decrease in the material removal and an increase in k_{iw} . As regards T_w , it increases in endothermic reactions and decreases in exothermic reactions.

By considering the ignition and extinction temperatures, it is not difficult to show that taking reversibility into account leads to a certain increase in their values.

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